Electronic Supplementary Information

Investigation on the vibrational and structural properties of a self-structured bridged silsesquioxane

Gaëlle Creff,^{*a*} Guilhem Arrachart,^{*b*} Patrick Hermet, ^{*a*} Hubert Wadepohl,^{*c*} Robert Almairac,^{*a*} David Maurin,^{*a*} Jean-Louis Sauvajol,^{*a*} Carole Carcel,^{*b*} Joël J. E. Moreau,^{*b*} Philippe Dieudonné, ^{*a*} Michel Wong Chi Man^{*,*b*} and Jean-Louis Bantignies^{*,*a*}

^aLaboratoire Charles Coulomb (UMR CNRS 5521), Université Montpellier 2, 34095 Montpellier Cedex 5, France ^bLaboratoire Architectures Moléculaires et Matériaux Nanostructurés - ICG Montpellier (UMR 5253)

CNRS- UMII-ENSCM- UMI, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier cedex 5, France

^cAnorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Corresponding authors:

Michel.wong-chi-man@enscm.fr

Jean-louis.bantignies@univ-montp2.fr

Details of the crystal structure determination

The data was characterized by a relatively steep drop in intensity with increasing diffraction angle. The space group R-3 was assigned based on E statistics (mean $|E^2-1| = 0.957$ to 0.84 Å resolution) and systematic absences.¹ An initial structural model was obtained using the charge flip procedure in P1.²⁻⁴ Inspection of the electron density so obtained indicated the presence of threefold inversion axis symmetry in the unit cell and revealed the positions of the C. N and O atoms of the ureidopyrimidinone backbone. Difference Fourier syntheses, which were carried out in R-3 after least squares refinement of the partial structure indicated extensive disorder of the side chain bearing the tris(ethoxysilyl) group. Maximum entropy electron density synthesis, ^{5, 6} using the observed structure factor amplitudes, combined with phases from the model without the side chain, and a flat prior, gave distinct atomic maxima for the ureidopyrimidinone backbones. Rather diffuse electron density was apparent around the -3 axis (see figure 1c), which is obviously due to the disordered C₂H₄Si(OEt₃) side chains. Several maxima in this region can be assigned to partially occupied positions of the silicon atoms (which were not included in the model used to generate the phases). In addition, solvent of crystallization could be present. Attempts to model this disorder with various split-atom schemes did not give satisfactory results. For further calculations, hydrogen atoms were added to the ureidopyrimidinone moiety in calculated positions (refined riding). Refinement with anisotropic displacement parameters for the nonhydrogen atoms converged to $R(F) \approx 0.4$ when the C₂H₄Si(OEt₃) side chain was omitted from the model. Addition of this substituent to the model, with an internal geometry highly restrained to sensible values and with isotropic atomic displacement parameters, reduced R(F) to 0.26.^{7, 8} To try to obtain more reliable geometric parameters for the ureidopyrimidinone dimers, the electron density due to the disordered chain was treated with the BYPASS procedure, ⁹⁻¹¹ and so effectively removed from the data. ¹² Refinement of the non-disordered part of the structure against the modified F_{obs} converged to R(F) = $0.090, wR(F^2) = 0.2764, \text{GooF} = 0.953.$

References

- 1. We are aware that molecular crystals with apparent trigonal symmetry are often twinned (see for example: R. Herbst-Irmer, G. M. Sheldrick, *Acta Cryst.*, 1998, **B54**, 443). However, in the present case the typical warning signs for twinning a very low value of $|E^2-1|$ and an only slightly higher merging R_{int} value for the higher symmetric Laue group(s) (-3m1, -31m) were absent.
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- 12. We note that this procedure is not completely satisfactory, because of the large number of electrons involved and its deficiencies in treating the region where the "squeezed" side chain connects to the ordered part.